

# PATENT ABSTRACTS OF JAPAN

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**(54) SILICA COATING LIQUID FOR FORMING LOW DIELECTRIC  
CONSTANT AND SILICA COAT SUBSTRATE WITH LOW DIELECTRIC  
CONSTANT**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a silica coating liquid for forming low-dielectric constant with a dielectric constant as small as  $\leq 2.5$ , having low moisture absorbability and high mechanical strength.

SOLUTION: This coating liquid contains (A) at least one silicon compound selected from the group consisting of alkoxysilanes of the general formula (I):  $X_nSi(OR)^{4-n}$  and silane halides of the general formula (II):  $X_nSiX'^{4-n}$  and (B) an organic template material of the general formula (III):  $[R_1R_2R_3R_4N]^+Y^-$  (in these formulas, X is H, F, a 1-8C alkyl, fluorine-substituted alkyl, aryl or vinyl; R is H, a 1-8C alkyl, aryl or vinyl; X' is a halogen atom; n is an integer of 0-3; R<sub>1</sub> is a 1-20C hydrocarbon group; R<sub>2</sub> to R<sub>4</sub> are each H or a 1-20C hydrocarbon group and may be the same as R<sub>1</sub>; and Y is a halogen atom or OH).

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#### CLAIMS

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[Claim(s)]

[Claim 1] (A) Coating liquid for low dielectric constant silica system coat formation which comes to contain the organic template material expressed in the (B) following general formula (III) as one or more sorts chosen from the group which consists of a halogenation silane shown by the alkoxysilane and the following general formula (II) which are shown by the following general formula (I) of silicon compounds, and/or its hydrolyzate.

$X_nSi(OR)^{4-n}$  (I)  $X_nSiX'^{4-n}$  (II)  $[R_1R_2R_3R_4N]^+Y^-$  (III)

(X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

Moreover, carbon numbers may differ mutually or it may be the same, and H atom or a carbon number may be the hydrocarbon group of 1-20, and R<sub>1</sub> of the hydrocarbon group of 1-20, and R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be still the same as that of R<sub>1</sub>. Y shows a halogen atom or an OH radical.

[Claim 2] Coating liquid for low dielectric constant silica system coat formation according to claim 1 characterized by including the polysiloxane which is the reactant of one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown by the alkoxysilane and the following general formula (II) which are indicated to be the silicon compound (aforementioned [A]) and/or its hydrolyzate by the (C) following general formula (I) with (B) organic template agent and/or its hydrolyzate, and a silica system particle.

$X_nSi -- (OR)_4-n$  (I)  $X_nSiX'_4-n$  (II) (X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

[Claim 3] Furthermore, coating liquid for low dielectric constant silica system coat formation according to claim 1 or 2 characterized by including (D) easily decomposability resin.

[Claim 4] The easily decomposability resin (aforementioned [ D ]) is coating liquid for low dielectric constant silica system coat formation according to claim 3 characterized by constituting the mutual penetrating mold polymer constituent which became entangled with the silicon compound (aforementioned [ A ]) and/or its hydrolyzate, or the aforementioned (C) polysiloxane on chain level.

[Claim 5] The silicon substrate by which it comes to prepare a low dielectric constant silica system coat in a component front face and/or a PN-junction part between the wiring layers of multilayer-interconnection structure on a silicon substrate, It is the semi-conductor substrate with a low dielectric constant silica system coat which consists of a multilayer wiring layer on a silicon substrate, and a low dielectric constant silica system coat. The semi-conductor substrate with a low dielectric constant silica system coat characterized by carrying out baking processing and being obtained after a low dielectric constant silica system coat applies the coating liquid for low dielectric constant silica system coat formation according to claim 1 to 4 and subsequently heat-treats it.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Specific inductive capacity of this invention is as small as 2.5 or less, and it relates to the semi-conductor substrate with which the low dielectric constant silica system coat this coat which has the coating liquid and such a property for forming the low dielectric constant silica system coat which moreover has low-water-flow part adsorbent and the property of high coat reinforcement was formed.

[0002]

[Background of the Invention] Since metal wiring spacing becomes narrow with high integration of a semiconductor device in the semiconductor device below the 0.25-micron

Ruhr which has a multilayer interconnection, the impedance of metal wiring by electrostatic induction increases, and we are anxious about the delay of a speed of response, increase of power consumption, etc. For this reason, to make as small as possible specific inductive capacity of the interlayer insulation film prepared between a semi-conductor substrate and metal wiring layers, such as an aluminum wiring layer, or between metal wiring layers is needed.

[0003] The interlayer insulation film used for the above purpose is formed on the semi-conductor substrate by the applying method which generally forms an insulator layer using vapor growth, such as a CVD method, or the coating liquid for coat formation. However, in vapor growth, such as a CVD method, that 3.5 of the fluorine dope silica film is called limitation, and the specific inductive capacity of the silica system coat obtained forms three or less silica system coat has the problem of being difficult. Moreover, adhesion with a coated side is bad, and adhesion with the resist ingredient used for micro processing also has it, and the coat formed using CVD coats and these coating liquid, such as poly aryl resin, fluoridation polyimide resin, and fluoro-resin, has problems, such as being further inferior to chemical resistance, oxygen-proof plasma nature, etc., although specific inductive capacity becomes 2 order. [ bad ]

[0004] In the coating liquid for silica system coat formation which contains the partial hydrolysate or hydrolyzate of the alkoxysilane or the halogenation silane used from the former further again, although the coat before and behind 2.5 is obtained for specific inductive capacity, there is a problem that adhesion with a coated side is bad. If the coating liquid for low dielectric constant silica system coat formation as shown below is used when this invention persons inquire wholeheartedly in order to solve these problems, they would find out that the coat which whose specific inductive capacity was as small as three or less, was moreover excellent in chemical resistance, such as adhesion with a coated side, a mechanical strength, and alkali resistance, or crack-proof nature, and was further excellent also in process compatibility, such as oxygen-proof plasma nature and etching workability, could be formed, and will have applied for these invention.

(1) Invention -1 (refer to JP,9-315812,A).

[0005] Coating liquid for low dielectric constant silica system coat formation containing alkoxysilane and/or halogenation silanes or such hydrolyzates, and a reactant with a silica particle.

(2) Invention -2 (refer to international application PCT/JP99 / 04051 official reports)  
Coating liquid for low dielectric constant silica system coat formation containing alkoxysilane and/or halogenation silanes or such hydrolyzates, and the readily decomposable resin that decomposes or vaporizes at the temperature of 500 degrees C or less.

(3) Invention -3 (refer to international application PCT/JP99 / 04050 official reports)  
Coating liquid for low dielectric constant silica system coat formation containing the polysiloxane which is the reactant of alkoxysilane and/or halogenation silanes or such hydrolyzates, and a silica particle, and the readily decomposable resin which decomposes or vaporizes at the temperature of 500 degrees C or less.

[0006] Then, although the coat which has the aforementioned property was obtained when this invention persons repeated these coating liquid and the trial which forms a low dielectric constant silica system coat on various semi-conductor substrates using the well-known coat forming method conventionally and performed it, specific inductive capacity

was 2.5 or less, water-adsorption nature was low and forming stably the coat which has the outstanding property that coat reinforcement is high found out the difficult thing. [0007] And when this invention persons continued research further wholeheartedly and the low dielectric constant silica system coat was formed on the semi-conductor substrate using the coating liquid for low dielectric constant silica system coat formation which comes to contain (B) organic template agent with one or more sorts of silicon compounds chosen from the group which consists of (A) alkoxysilane and a halogenation silane, and/or the hydrolyzate of those, they find out that the above problems are easily solvable, and came to complete this invention.

[0008]

[Objects of the Invention] Without giving a damage to metal wiring which this invention tends to solve the above troubles and was arranged on the semi-conductor substrate The coating liquid for low dielectric constant silica system coat formation and this coating liquid which can form the low dielectric constant silica system coat which specific inductive capacity is as small as 2.5 or less, is moreover low-water-flow part adsorbent, and has the outstanding property of having high coat reinforcement are applied. It aims at offering the semi-conductor substrate with which the low dielectric constant silica system coat obtained by carrying out desiccation etc. was formed.

[0009]

[Summary of the Invention] The coating liquid for low dielectric constant silica system coat formation of this invention is coating liquid for low dielectric constant silica system coat formation which comes to contain one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown by the alkoxysilane and the following general formula (II) which are shown by the (A) following general formula (I) and/or its hydrolyzate, and (B) organic template agent.

[0010] (B) Coating liquid for low dielectric constant silica system coat formation which comes to contain the organic template material expressed with the following general formula (III).

$X_nSi(OR)_{4-n}$  (I)  $X_nSiX'_{4-n}$  (II)  $[R_1R_2R_3R_4N]^+Y^-$  (III)

(X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

[0011] Moreover, carbon numbers may differ mutually or it may be the same, and H atom or a carbon number may be the hydrocarbon group of 1-20, and R1 of the hydrocarbon group of 1-20, and R2, R3 and R4 may be still the same as that of R1. Y shows a halogen atom or an OH radical.

Said coating liquid for low dielectric constant silica system coat formation is characterized by including the polysiloxane which is the reactant of one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown by the alkoxysilane and the following general formula (II) which are indicated to be the silicon compound (aforementioned [ A ]) and/or its hydrolyzate by the (C) following general formula (I) with (B) organic template agent and/or its hydrolyzate, and a silica system particle.

[0012]  $X_nSi -- (OR)_{4-n}$  (I)  $X_nSiX'_{4-n}$  (II) (X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl

group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

It is desirable that (D) easily decomposability resin is further contained in the coating liquid for low dielectric constant silica system coat formation concerning this invention.

[0013] As for such (D) easily decomposability resin, it is desirable to constitute the mutual penetrating mold polymer constituent which became entangled with (A) silicon compound and/or its hydrolyzate, or the (C) polysiloxane on chain level. The semi-conductor substrate with a low dielectric constant silica system coat of this invention The silicon substrate by which it comes to prepare a low dielectric constant silica system coat in a component front face and/or a PN-junction part between the wiring layers of multilayer-interconnection structure on a silicon substrate, It is the semi-conductor substrate with a low dielectric constant silica system coat which consists of a multilayer wiring layer on a silicon substrate, and a low dielectric constant silica system coat, and after a low dielectric constant silica system coat applies said coating liquid for low dielectric constant silica system coat formation and subsequently heat-treats it, it is characterized by carrying out baking processing and being obtained.

[0014]

[Detailed Description of the Invention] Hereafter, the coating liquid for low dielectric constant silica system coat formation of this invention is explained concretely.

One or more sorts of silicon compounds chosen from the group which consists of (A) alkoxysilane and a halogenation silane and/or its hydrolyzate, and (B) organic template material are distributing or dissolving the coating liquid for low dielectric constant silica system coat formation by [coating liquid for low dielectric constant silica system coat formation] this invention in water and/or an organic solvent.

[0015] (A) One or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown by the alkoxysilane and the following general formula (II) which are shown by the following general formula (I) as a silicon compound, its hydrolyzate silicon compound, and its hydrolyzate, and/or its hydrolyzate are used.

$X_nSi(OR)_{4-n}$  (I)  $X_nSiX'_{4-n}$  (II) (X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

As an example of alkoxysilane shown by said general formula (I) Methyl trimethoxysilane, methyl triethoxysilane, a methyl triisopropoxy silane, Ethyltrimethoxysilane, ethyltriethoxysilane, an ethyl triisopropoxy silane, Octyl trimethoxysilane, octyl triethoxysilane, vinyltrimethoxysilane, Vinyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, Trimethoxysilane, triethoxysilane, a triisopropoxy silane, Fluoro trimethoxysilane, fluoro triethoxysilane, dimethyldimethoxysilane, Dimethyl diethoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, Dimethoxysilane, diethoxysilane, difluoro dimethoxysilane, difluoro diethoxysilane, trifluoromethyl trimethoxysilane, trifluoromethyl triethoxysilane, etc. are mentioned.

[0016] As an example of the halogenation silane shown by said general formula (II), trichlorosilane, a TORIBUROMO silane, dichlorosilane, fluoro trichlorosilane, a fluoro

BUROMO silane, methyltrichlorosilane, ethyl trichlorosilane, phenyl trichlorosilane, vinyl trichlorosilane, etc. are mentioned. In the above, when using the hydrolyzate of alkoxysilane and/or a halogenation silane In the organic solvent solution of alkoxysilane and/or a halogenation silane The Si-OR radical which constitutes alkoxysilane for water required for a hydrolysis reaction, Or per [ which constitutes a halogenation silane ] one mol of Si-X' radicals, it adds in the amount of 0.1-2 mols preferably, and 0.1-5 mols of catalysts are usually added if needed in the amount of 0.001-1 mol per alkoxysilane or one mol of halogenation silanes. Hydrolyzate may be a partial hydrolysate by which the part was hydrolyzed, even if it hydrolyzes completely.

[0017] As an organic solvent in the case of using such alkoxysilane and a halogenation silane Alcohols, ketones, ether, ester, and hydrocarbons are mentioned. More specifically For example, alcohols, such as a methanol, ethanol, propanol, and a butanol, Ketones, such as a methyl ethyl ketone and methyl isobutyl ketone, methyl cellosolve, Glycol ether, such as ethylcellosolve and the propylene glycol monopropyl ether Glycols, such as ethylene glycol, propylene glycol, and hexylene glycol Aromatic hydrocarbon, such as hydrocarbons, such as ester, such as methyl acetate, ethyl acetate, methyl lactate, and ethyl lactate, a hexane, a cyclohexane, and an octane, toluene, a xylene, and a mesitylene, is mentioned.

[0018] As a catalyst, the compound in which acidity is shown in water solutions, such as organic acids, such as inorganic acids, such as a hydrochloric acid, a nitric acid, and a sulfuric acid, an acetic acid, oxalic acid, and toluenesulfonic acid, or metal soap, is mentioned. As hydrolysis conditions, when hydrolyzing alkoxysilane, 80 degrees C or less of reaction temperature are 5-60 degrees C preferably, and reaction time is usually 0.5 - 5 hours preferably under stirring conditions for 10 or less hours. Moreover, when hydrolyzing a halogenation silane, 50 degrees C or less of reaction temperature are 5-20 degrees C preferably, and reaction time is usually 1 - 10 hours preferably under stirring conditions for 20 or less hours. Furthermore, when hydrolyzing alkoxysilane and a halogenation silane to coincidence, the hydrolysis conditions of a halogenation silane are usually adopted.

[0019] Thus, it is desirable 500-10,000, and for the obtained hydrolyzate or the partial hydrolysis significant work mean molecular weight (polystyrene conversion) to be in the range of 1,000-5,000 preferably. Its coating nature is also good while it passes through the coating liquid which will be obtained if hydrolyzate or partial hydrolysis significant work average molecular weight is in said range and it is excellent in the Tokiyasu quality.

[0020] A such silicon compound and its hydrolyzate are SiO<sub>2</sub> conversions, and it is desirable to be preferably contained in 10 - 25% of the weight of the range five to 40% of the weight in coating liquid.

(B) organic template material -- next as organic template material used for this invention, what is expressed with the following general formula (III) is mentioned.

[0021]

[R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>N]+Y- (III)

Among a formula, carbon numbers may differ mutually or it may be the same, and H atom or a carbon number may be the hydrocarbon group of 1-20, and R<sub>1</sub> of the hydrocarbon group of 1-20, and R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be still the same as that of R<sub>1</sub>. Y shows a halogen atom or an OH radical.

[0022] Such organic template material is easily removed by heat-treatment after silica

system coat formation. For this reason, after organic template material is removed, the pore of uniform magnitude comparable as organic template material is formed into a silica system coat, and the silica system coat of a low dielectric constant and high coat reinforcement can be obtained. As such organic template material, specifically Tetraethylammonium hydroxide, a tetraethylammonium star's picture, Tetraethyl ammoniumchloride, tetrapropylammonium hydroxide, A tetrapropylammonium star's picture, tetrapropylammonium chloride, n-hexadecyl trimethylammonium hydroxide, n-hexadecyl trimethylammonium star's picture, n-octadecyl trimethylammonium hydroxide, n-octadecyl trimethylammonium star's picture, etc. can be mentioned.

[0023] If Y uses the organic template material (it becomes an organic base in this case) which is an OH radical, in order to act also as said alkoxysilane in coating liquid and/or a halogenation silane, or a condensation catalyst of such hydrolyzates, when bridge formation progresses and alkoxysilane and/or halogenation silanes, or such hydrolyzates have End SiH especially, conversion is effectively carried out to precise polysiloxane structure, and the silica system coat which has high coat reinforcement is obtained.

[0024] As for the amount of such organic template material used, it is desirable that it is in 10 - 200% of the weight of the range of the weight when converting the silica system component in coating liquid into SiO<sub>2</sub>. When the amount of the organic template material used is less than 10 % of the weight, it becomes inadequate forming [ of the pore of magnitude comparable as organic template material ], and a silica system coat with a dielectric constant low enough may not be obtained.

[0025] When the amount of the organic template material used exceeds 200 % of the weight, it is in the inclination for the reinforcement of the silica system coat which formation of pore increases too much and is obtained to fall.

(C) a polysiloxane -- it is desirable that the polysiloxane which is the reactant of one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown in such coating liquid for low dielectric constant silica system coat formation by the alkoxysilane and the following general formula (II) which are further shown by the following general formula (I) and/or such hydrolyzates, and a silica system particle is included.

[0026]  $X_nSi(OR)_{4-n}$  (I)  $X_nSiX'_{4-n}$  (II) (X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

A silica system particle can mix more than a kind of the alkoxysilane of said general formula (I) to an organic solvent, and can obtain it hydrolysis and by carrying out condensation polymerization under existence of water and ammonia. As alkoxysilane expressed with a general formula (I), what was illustrated in the silicon compound (aforementioned [ A ]) and its hydrolyzate, and the same thing are mentioned.

[0027] When the method of preparation of a silica system particle is further explained to a detail, stirring a water-alcoholic mixed solvent, alkoxysilane and aqueous ammonia are added to this mixed solvent, and there is a method of making the hydrolysis reaction of an alkoxy run cause etc., for example. Under the present circumstances, 0.5-50 mols per one mol of Si-OR radicals of water which constitute alkoxysilane are used in an amount which becomes 1-25 mols preferably.



[0028] Moreover, when alkoxysilane is converted into  $\text{SiO}_2$ , as for ammonia, it is desirable to blend 0.01-1 mol to one mol of alkoxysilane in an amount which becomes 0.05-0.8 mols preferably. As for the hydrolysis reaction of an alkoxy run, it is desirable to carry out using heat-resistant proof-pressure containers, such as an autoclave, above 200 degrees C preferably 180 degrees C or more. Furthermore, it can also ripe at the same temperature or higher temperature after this. The polycondensation of alkoxysilane is promoted more for the higher one, and above-mentioned reaction temperature and/or maturing temperature become precise [ the interior of a silica system particle ]. If reaction and/or aging are performed at such temperature, a silica system particle becomes much more precise, and the residual functional group on the front face of a particle will also decrease at the same time the hygroscopicity of the particle itself falls.

[0029] Moreover, the solvent of high-boiling points, such as ethylene glycol, is added, for example to the water-alcoholic mixed solvent under stirring, alkoxysilane is hydrolyzed, and a silica system particle may be generated and may be grown up. If the solvent of such a high-boiling point is added at the time of hydrolysis of alkoxysilane, the ester exchange reaction of an alkoxy group will occur, a high-boiling point solvent will be incorporated inside a silica particle, and a porous silica system particle will be obtained.

[0030] As other silica system particles, the silica sol obtained by the ion exchange, hydrolysis, etc. in alkali-metal silicate etc. is used. Furthermore, the particle which consists of a porosity zeolite which removed aluminum from the zeolite which consists of an aluminosilicate can also be used. As for the silica system particle used by this invention, it is desirable for 5-50nm of the mean particle diameter to be within the limits of 10-50nm preferably. As long as it is the particle of the particle size which is within the limits of this, the things of a uniform particle size may also be two or more kinds of mixture of a particle with which particle size differs. Moreover, it may be a globular form or you may be an anomaly. It is easy to produce a defect at the time of micro processing in the micro photolithography process of a coat that this particle size will be obtained from the coating liquid manufactured from this by the stability of the coating liquid manufactured from this with the passage of time becoming scarce in less than 5nm if 50nm is exceeded on the other hand.

[0031] The polysiloxane used by this invention mixes one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane expressed with the alkoxysilane and the above-mentioned general formula (II) which are expressed with such a silica system particle and the above-mentioned general formula (I) in an organic solvent, and is obtained by making it hydrolyze under existence of water and a catalyst. As a halogenation silane expressed with the alkoxysilane expressed with a general formula (I), and a general formula (II), what was illustrated in the silicon compound (aforementioned [ A ]) and its hydrolyzate, and the same thing are mentioned.

[0032] Such a preparation approach of a polysiloxane can be prepared according to the approach indicated by official reports, such as said invention -1 (refer to JP,9-315812,A) for which these people applied, or said invention -3 (international application PCT/JP99/04050 reference). One or more sorts of the halogenation silane specifically shown by the alkoxysilane shown by the above-mentioned silica system particle and the general formula (I) and the general formula (II) are mixed in an organic solvent, and it is obtained by performing the hydrolysis reaction of alkoxysilane and a halogenation silane under existence of water and a catalyst.

[0033] As alkoxysilane shown by said general formula (I), what was illustrated by said silica system particle, and the same thing are mentioned. The alkoxysilane used for hydrolysis may be the same as what was used at the time of silica system particle preparation, or may differ. As an organic solvent, the aromatic hydrocarbon other than what was illustrated by preparation of said silica system particle, and the same thing, such as hydrocarbons, such as a hexane, a cyclohexane, and an octane, toluene, a xylene, and a mesitylene, is mentioned.

[0034] As a catalyst, the compound in which acidity is shown in water solutions, such as organic acids, such as inorganic acids, such as a hydrochloric acid, a nitric acid, and a sulfuric acid, an acetic acid, oxalic acid, and toluenesulfonic acid, or metal soap, is mentioned. Water required for the hydrolysis reaction of an ARUKO gardenia fruit run or a halogenation silane hits one mol (when mixing and using alkoxysilane and a halogenation silane, it is the sum total of a Si-OR radical and a Si-X radical) of Si-X radicals which constitute one mol of Si-OR radicals and halogenation silane which constitutes alkoxysilane, and it is usually desirable to be preferably used in the amount of 0.1-2 mols 0.1-5 mols. Moreover, as for a catalyst, it is desirable to be added in the amount of 0.001-1 mol per alkoxysilane or one mol (it is the total quantity when mixing and using alkoxysilane and a halogenation silane) of halogenation silanes.

[0035] Both the mixed rates (S/T) of the alkoxysilane and/or the halogenation silane (T) which are shown by the silica system particle (S) used for preparation of a polysiloxane and said general formula (I) are the weight ratios when converting SiO<sub>2</sub>, and it is desirable 1 / 99 - 10/90, and that it is in the range of 1 / 99 - 5/95 preferably. The stability of the polysiloxane from which a hydrolysis reaction advances and this mixed rate (S/T) is obtained less than by 1/99 besides the front face of a silica system particle with the passage of time may become scarce. Moreover, when there are more these mixed rates (S/T) than 10/90, the bonding strength of the polysiloxane obtained becomes weak and there is an inclination it becomes impossible to maintain sufficient film reinforcement.

[0036] Although especially the reaction condition in this process is not restricted, about 100 degrees C or less, it is usually desirable [ it is 80 degrees C or less in temperature preferably, and / agitating ] to carry out over 0.5 - 3 hours preferably for 0.5 to 5 hours. Thereby, the polysiloxane to which the hydrolyzate of alkoxysilane or a halogenation silane reacted to the front face of a silica system particle is obtained.

[0037] However, about the preparation approach of this polysiloxane, it is not limited above and the polysiloxane manufactured by the approach given in JP,9-315812,A etc. can also be used.

(D) The coating liquid for low dielectric constant silica system coat formation concerning easily decomposability resin this invention may contain easily decomposability resin further.

[0038] It decomposes or vaporizes by having the number average molecular weight (polystyrene conversion) of 500-50,000 as easily decomposability resin, irradiating heat treatment or ultraviolet rays, infrared radiation, an electron ray, and an X-ray at the temperature of 500 degrees C or less, or irradiating the oxygen plasma. as the example of such easily decomposability resin -- number average molecular weight (polystyrene conversion) -- 500-50,000 -- the cellulose system resin of 5,000-30,000, polyamide system resin, polyester system resin, acrylic resin, polyether system resin, polyolefine system resin, polyol system resin, epoxy system resin, etc. are mentioned preferably.

[0039] Moreover, in the coating liquid for low dielectric constant silica system coat formation of this invention, it is desirable to constitute the mutual penetrating mold polymer constituent with which the easily decomposability resin (aforementioned [ D ]) became entangled with the silicon compound (hydrolyzate) (aforementioned [ A ]) or the aforementioned (C) polysiloxane on chain level. It is desirable 500-50,000, and for the number average molecular weight (polystyrene conversion) of such a mutual penetrating mold polymer constituent to be in the range of 1,000-30,000 preferably.

[0040] The detail is indicated by the official report of the invention -2 (international application PCT/JP 99/04051) for which these people applied, or said invention -3 (international application PCT/JP 99/04050) about the preparation approach of such a mutual penetrating mold polymer constituent. Such a polymer constituent can be prepared by mixing the silicon compound (hydrolyzate) (aforementioned [ A ]) and/or the (C) polysiloxane, and (D) easily decomposability resin in organic solvents, such as ketones, ether, ester, hydrocarbons, and aromatic hydrocarbon. In this case, in this organic solvent, one sort of the alkoxysilane shown by said general formula (I) if needed or two sorts or more can be added.

[0041] (A) As for the solution (dispersion liquid) which mixed a silicon compound (hydrolyzate), and/or the (C) polysiloxane and (D) easily decomposability resin, it is desirable under existence of little water and an acid catalyst to stir at the temperature of 20-60 degrees C for 1 to 6 hours. The secondary hydrolysis reaction of (A) silicon compound (hydrolyzate) and/or a polysiloxane advances in an easily decomposability resin frame by this, and the polymer constituent with which (A) silicon compound (hydrolyzate) and/or the (C) polysiloxane, and (D) easily decomposability resin became entangled with homogeneity is obtained. However, in this approach, the polymer constituent which became entangled with homogeneity according to the class of easily decomposability resin etc. may not be obtained.

[0042] Moreover, a polymer constituent can be prepared alkoxysilane or a halogenation silane, easily decomposability resin, and if needed by carrying out a contact hydrolysis reaction using the organic solvent and water which do not dissolve a silica system particle. According to this preparation approach approach, a mutual penetrating mold polymer constituent can be formed easily directly. As for the coating liquid of this invention, it is desirable to contain preferably solid content, such as the silicon compound (for it to be the same after containing also in hydrolyzate) (aforementioned [ A ]) shown above, the organic template material (aforementioned [ B ]) and the arbitrary and included aforementioned (C) polysiloxane, a constituent containing the easily decomposability resin (aforementioned [ D ]), and the above mentioned mutual penetrating mold polymer constituent, in 10 - 30% of the weight of the amount five to 35% of the weight in an organic solvent.

[0043] It can be used as said organic solvent, choosing from organic solvents, such as alcohols, glycol ether, ketones, ether, ester, hydrocarbons, and aromatic hydrocarbon. Below, the semi-conductor substrate with a low dielectric constant silica system coat of this invention is explained concretely.

[0044] The semi-conductor substrate with a low dielectric constant silica system coat concerning [semi-conductor substrate with low dielectric constant silica system coat] this invention The silicon substrate by which it comes to prepare a low dielectric constant silica system coat in a component front face and/or a PN-junction part between the wiring

layers of multilayer-interconnection structure on a silicon substrate, It is the semi-conductor substrate with a low dielectric constant silica system coat which consists of a multilayer wiring layer on a silicon substrate, and a low dielectric constant silica system coat, and after a low dielectric constant silica system coat applies said coating liquid for low dielectric constant silica system coat formation and subsequently heat-treats it, it is characterized by carrying out baking processing and being obtained.

[0045] The silica system coat formed on this silicon substrate has specific inductive capacity as small as 2.5 or less, moreover is excellent in chemical resistance, such as adhesion with a coated side, and alkali resistance, or crack-proof nature, and it not only also has process compatibility, such as oxygen-proof plasma nature and etching workability, further, but it has remarkable low water adsorption nature and coat reinforcement high enough.

[0046] This low dielectric constant silica system coat applies the above mentioned coating liquid for low dielectric constant silica system coat formation, is formed, and consists of a silica system component which uses as a precursor hydrolyzate of one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown by the alkoxysilane and the following general formula (II) which are shown by the following general formula (I).

$\text{XnSi} \text{--} (\text{OR})_{4-n}$  (I)  $\text{XnSiX}'_{4-n}$  (II) (X expresses a hydrogen atom, a fluorine atom or the alkyl group of carbon numbers 1-8, a fluorine permutation alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of carbon numbers 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

As an example of the halogenation silane shown by the alkoxysilane shown by said general formula (I), and said general formula (II), the same thing is mentioned with having described above.

[0047] The polysiloxane which is the reactant of the hydrolyzate of one or more sorts of silicon compounds chosen from the group which consists of a halogenation silane shown by the alkoxysilane shown by said general formula (I) and said general formula (II), and a silica system particle may be included in such a silica system coat. It is desirable that such a polysiloxane is included in 5 - 90% of the weight of the range by oxide ( $\text{SiO}_2$ ) conversion in a coat. It is 20 - 80% of the weight of the range still more preferably. If the polysiloxane is included in said range, the specific inductive capacity of a coat can obtain the silica system coat excellent in thermal resistance, reinforcement, etc. or less by 2.5.

[0048] In addition, with heating at the time of coat formation, it vaporized or decomposed and the organic template material and easily decomposability resin which were added by coating liquid have disappeared. Next, it illustrates concretely about the formation approach of the low dielectric constant silica system coat on a semi-conductor substrate. formation of a low dielectric constant silica system coat -- especially -- a limit -- there is nothing -- a conventionally well-known approach -- being employable -- for example, (a) -- the above coating liquid for low dielectric constant silica system coat formation is applied on a semi-conductor substrate, and after heat-treating the coat (b) obtained at the temperature of 350 degrees C or less, it can form by carrying out baking processing of the (c) this coat at the temperature of 350-450 degrees C under the ambient atmosphere of inert gas.

[0049] (a) Although the spin coat method, the dip coating method, the roll coat method,

the decalcomania method, etc. are adopted as the general spreading process as the method of application of such coating liquid, also in this invention approach, the coating liquid for low dielectric constant silica system coat formation can be conventionally applied on a semi-conductor substrate using such a well-known approach.

[0050] (b) 350 degrees C or less of coats applied on heat-treatment, thus a semi-conductor substrate are preferably heat-treated at the temperature of 50-300 degrees C. Although this heating changes with thickness of a coat etc., it is desirable to carry out over 2 - 5 minutes preferably for 1 to 10 minutes. Although this heat-treatment may be performed under inert gas ambient atmospheres, such as nitrogen, like before, it is desirable to carry out under an air ambient atmosphere. This is because the damage by metal oxidization etc. is not given to metal wiring arranged on the semi-conductor substrate even if it heat-treats under the air ambient atmosphere in which this processing is that of short-time \*\*\*\*\* under the comparatively low temperature conditions of 350 degrees C or less, and contains oxygen comparatively so much even if. SiO<sub>2</sub> to which bridge formation of Si-O-Si association progressed on the occasion of latter (c) baking processing since possibility that could reduce the amount of the expensive nitrogen gas used by this, and the oxygen of a minute amount would be incorporated in a coat increased It generates and becomes easy to form the low dielectric constant silica system coat which has low-water-flow part adsorbent and high coat reinforcement.

[0051] While the organic solvent contained in a coat by heat-treating as mentioned above evaporates, organic template material \*\*\*\*s, and while the polymerization of a formed element progresses on the other hand and hardening, the reflow nature of a coat increases by the melt viscosity of a polymer falling in process of heating, and the surface smoothness of the coat obtained improves. Thus, although the thickness of the low dielectric constant silica system coat formed changes also with the semi-conductor substrate which forms a coat, or its purposes, on the silicon substrate in a semiconductor device, it is about 100-600nm, and, in between the wiring layers of a multilayer interconnection, is usually 100-1,000nm, for example.

[0052] (c) baking \*\*\*\* -- as for the coat to which said heat-treatment was performed, subsequently, it is desirable under the ambient atmosphere of inert gas to carry out baking processing (cure) at the temperature of 350-450 degrees C. As said inert gas, desirably, using nitrogen gas may add oxygen gas or air to this if needed further, and it may use as inert gas containing a small amount of oxygen.

[0053] Although the aforementioned burning temperature changes with descriptions of Si content compound (silica system component) contained in the class of organic template material used for coating liquid, an amount, or coating liquid etc., it is chosen from a 350-450-degree C temperature requirement. if it is this temperature requirement -- low-water-flow part adsorbent -- low dielectric constant silica system coat \*\*\*\* of high coat reinforcement -- things are made. Furthermore, also when the coating liquid containing easily decomposability resin is used, it is required to carry out at the above temperature to which this easily decomposability resin decomposes or vaporizes, and if it is the temperature requirement which is 350-450 degrees C, the low dielectric constant silica system coat of high intensity will be formed by the low consistency in which a matrix has only the hole of a diameter 5nm or less substantially with organic template material and/or easily decomposability resin.

[0054] Moreover, although this baking processing changes with the class of coating

liquid, thickness of a coat, etc., it is desirable to carry out over 10 - 60 minutes. since aluminum wiring, copper wiring, etc. which constitute a semi-conductor substrate oxidize, or melting be carry out and damage may be do to this wiring layer when the coat which have sufficient coat reinforcement be obtain and the temperature of baking processing exceed 450 degrees C here, since bridge formation of the precursor of a silica system component cannot progress easily, if the temperature of baking processing be less than 350 degrees C, as for the temperature concerned, it be desirable to maintain at the range of 350-450 degrees C.

[0055]

[Effect of the Invention] The coating liquid for low dielectric constant silica system coat formation of this invention serves as a precursor of a specific silica system component, and organic template material from easily decomposability resin if needed, and bridge formation of a silica system component precursor advances, and although the coat obtained is a low consistency in porosity, it can obtain the low dielectric constant silica system coat of high coat reinforcement.

[0056] The semi-conductor substrate with a low dielectric constant silica system coat of this invention Into a component front face and/or a PN-junction part between the wiring layers of multilayer-interconnection structure on a silicon substrate The coat which are the components for semiconductor devices with which the low dielectric constant silica system coat was formed, and was formed on this semi-conductor substrate Since it is formed using the coating liquid for low dielectric constant silica system coat formation of this invention, adhesion with a coated side, It excels in chemical resistance, such as alkali resistance, or crack-proof nature, and it not only also has process compatibility, such as oxygen-proof plasma nature and etching workability, further, but has remarkable low water adsorption nature and coat reinforcement high enough.

[0057]

[Example] Hereafter, although an example explains this invention, this invention is not limited to these examples.

[0058]

[Example 1] Hydrolysis of triethoxysilane and methyl trimetoxysilane was performed at the temperature of 20 degrees C for about 1 hour, having held the mixed solution (preparation triethoxysilane (Shin-Etsu Chemical make) 80.0g of the coating liquid for coat formation (S-1), methyl trimetoxysilane (Shin-Etsu Chemical make) 68.18g, and ethanol 451.82g) at 20 degrees C, having added 54.0g of nitric-acid content water solutions of concentration to this at once 0.05% of the weight, and stirring at the rate of 150rpm. Then, the propyl propylene glycol (PFG) of an amount was added 1.5 times, the solvent permutation was carried out at propyl propylene glycol (PFG) using the rotary evaporator, the alcohol generated by the hydrolysis reaction and the moisture (a nitric acid is included) which dissolved were removed completely, and the hydrolyzate (matrix precursor PFG dispersion liquid) of the triethoxysilane whose silica concentration is 20 % of the weight, and methyl trimetoxysilane was obtained.

[0059] To 100g of the PFG solution of the matrix precursor obtained as mentioned above, 25g of methanol solution of n-hexadecyl trimethylammonium hydro KISAIDO (n-HDTMAH) of 20 % of the weight of concentration was mixed as organic template material, and 125g (S-1) of coating liquid for coat formation was obtained to it. The coating liquid for coat formation (S-1) which is the manufacture above of a semi-

conductor substrate with a silica system coat (L-1), and was made and prepared was applied to the 8 inches silicon wafer (semi-conductor substrate) with the spin coat method, respectively.

[0060] Then, heating down stream processing was presented with the substrate, and it was heated for 3 minutes at the temperature of 150 degrees C under the air ambient atmosphere. In this heat-treatment, since the organic solvent contained in a coat evaporated, this was exhausted out of the system. Subsequently, under nitrogen-gas-atmosphere mind, baking processing for 30 minutes was performed at the temperature shown in Table 1, and the semi-conductor substrate with a silica system coat (L-1) was manufactured. Next, it cooled to the temperature near the room temperature, and took out out of the system.

[0061] Thus, the thickness of the obtained coat was 5,000A. Subsequently, the existence (a wiring resistance value change is measured with a circuit tester) of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity (the mercury probe method, frequency of 1MHz) of the obtained silica system coat and the coat before and behind an oxygen plasma exposure (the TDS method: Thermal Desorption Mass-Spectroscopy), coat reinforcement (Sebastian strength test machine), and a substrate was measured.

[0062] A result is shown in Table 1.

[0063]

[Example 2] To 100g of PFG dispersion liquid of the matrix precursor prepared like the preparation example 1 of the coating liquid for coat formation (S-2), 75g of methanol solution of n-hexadecyl trimethylammonium hydro KISAIDO of 20 % of the weight of concentration was mixed as organic template material, and 175g (S-2) of coating liquid for coat formation was obtained to them.

[0064] The semi-conductor substrate with a silica system coat (L-2) was manufactured like the example 1 except having used each coating liquid for coat formation (S-2) which is the manufacture above of a semi-conductor substrate with a silica system coat (L-2), and was made and prepared. The thickness of the obtained coat was 5,000A. Subsequently, the existence of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat reinforcement, and a substrate was measured.

[0065] A result is shown in Table 1.

[0066]

[Example 3] In 80g of PFG solutions of the matrix precursor prepared like the preparation example 1 of the coating liquid for coat formation (S-3), 20g of PFG solutions of acrylic resin (number average molecular weight is 22,190) of 20 % of the weight of concentration was mixed, subsequently to this, 20g of methanol solution of n-hexadecyl trimethylammonium hydro KISAIDO (n-HDTMAH) of 20 % of the weight of concentration was mixed as organic template material in them, and 120g (S-3) of coating liquid for coat formation was obtained in them.

[0067] The semi-conductor substrate with a silica system coat (L-3) was manufactured like the example 1 except having used each coating liquid for coat formation (S-3) which is the manufacture above of a semi-conductor substrate with a silica system coat (L-3), and was made and prepared. The thickness of the obtained coat was 5,000A.

Subsequently, the existence of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat reinforcement, and a substrate was measured.

[0068] A result is shown in Table 1.

[0069]

[Example 4] In 66.67g of PFG dispersion liquid of the matrix precursor prepared like the preparation example 1 of the coating liquid for coat formation (S-4), it is acrylic resin (number average molecular weight) of 20 % of the weight of concentration. 33.33g of PFG solutions of 22,190 is mixed. Subsequently, 16.67g of methanol solution of n-hexadecyl trimethylammonium hydro KISAIDO (n-HDTMAH) of 20 % of the weight of concentration was mixed as organic template material to this, and 116.67g (S-4) of coating liquid for coat formation was obtained.

[0070] The semi-conductor substrate with a silica system coat (L-4) was manufactured like the example 1 except having used the coating liquid for coat formation (S-4) which is the manufacture above of a semi-conductor substrate with a silica system coat (L-4), and was made and prepared. The thickness of the obtained coat was 5,000A. Subsequently, the existence of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity of a silica system coat and the coat before and behind an oxygen plasma exposure, coat reinforcement, and a substrate was measured.

[0071] A result is shown in Table 1.

[0072]

[Example 5] Except having used n-octadecyl trimethylammonium hydro KISAIDO (n-ODTMAH) as organic template material, the coating liquid for coat formation (S-5) was prepared like the example 4, and, subsequently the semi-conductor substrate with a silica system coat (L-5) was manufactured. The existence of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat reinforcement, and a substrate was measured.

[0073] A result is shown in a table.

[0074]

[The example 1 of a comparison] Except having not used organic template material, the coating liquid for coat formation was prepared like the example 1, and, subsequently the semi-conductor substrate with a silica system coat was manufactured. The existence of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat reinforcement, and a substrate was measured.

[0075] A result is shown in Table 1.

[0076]

[The example 2 of a comparison] Except having not used organic template material, the coating liquid for coat formation was prepared like the example 4, and, subsequently the semi-conductor substrate with a silica system coat was manufactured. The existence of damage to metal wiring on the amount change of water adsorption of the specific inductive capacity of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat reinforcement, and a substrate was measured.

[0077] A result is shown in Table 1.



[0078]  
[Table 1]

表 1

	被膜形成用塗布液										焼成工程 加熱温度 (℃)	被膜付基板の特性					
	マトリックス前駆体 分散液 重量(g)		有機テンプレート 種類		濃度 重量%		易分解性樹脂溶液					比誘 電率	水分吸 着量	被膜強 度 (Mpa)	金属配線 への損傷 の有無		
							種類	溶液 重量(g)	濃度 重量%	種類						溶液 重量(g)	濃度 重量%
実施例1	100	20	n-HDTMAH		25	20	-	-	-	-	425	2.5	少	>70	無		
実施例2	100	20	n-HDTMAH		75	20	-	-	-	-	425	2.0	少	50	無		
実施例3	80	20	n-HDTMAH		20	20			アクリル樹脂	20	20	425	2.3	少	60	無	
実施例4	66.67	20	n-HDTMAH		16.67	20			アクリル樹脂	33.33	20	425	2.1	少	55	無	
実施例5	66.67	20	n-ODTMAH		16.67	20			アクリル樹脂	33.33	20	425	2.0	少	50	無	
比較例1	100	20	使用せず						-	-	-	425	3.5	少	>70	無	
比較例2	66.67	20	使用せず						アクリル樹脂	33.33	20	500	3.3	多	>70	有	